PB-215 059

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Environmental Health Center
Cincinnati, Ohio

1 December 1949

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U. S. Public Health Service

ENVIRONMENTAL HEALTH CENTER

Research and Development Branch

Physics and Chemistry Section

Cincinnati, Ohio

December 1, 1949

TENTATIVE ANALYTICAL METHODS FOR CADMIUM, CHROMIUM, AND CYANIDE IN WATER

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Application of Dithizone in the Determination of Cadmium in Water Supplies

Diphenylthiocarbazone ($C_{13}H_{12}SN_4$), commonly referred to as dithizone, is known to react with a number of metals producing yellow-orange, red. or violet colored solutions. These complexes, which are soluble in $CHCl_3$ and to a lesser extent in CCl_4, are dissolved in the organic solvent and eventually removed by separating the heavier organic liquid from the aqueous phase. A solution of dithizone in pure CCl_4, which is dark green in color, becomes reddish orange when cadmium is present. The intensity of this color, when compared with standards, is an indication of the concentration of Cd present.

However, since dithizone produces similar color reactions with many salts, the interference that might be caused may largely be eliminated by controlling the conditions. Generally speaking, the methods usually employed to improve the selectivity of the dithizone reaction are:

(1) pH control

(2) Removal of interfering metals by the addition of complex forming reagents.

(3) Oxidation or reduction of the interfering metals.

In the presence of arsenic, bismuth, iron, lead, antimony, tin and zinc, the cadmium can be extracted from an alkaline solution of Rochelle salt. Where copper and cadmium are found together, their separation is accomplished with $Na_2S_2O_3$ which removes the Cu as a precipitate and keeps the Cd in solution as a complex.

The reagent is prepared by dissolving 50 mg. of dithizone in a liter of U.S.P. CCl_4. In the procedure for the Cd determination, 10 ml. of 10% NaOH and 2 ml. of 20% Rochelle salt are added to a 50 ml. water sample. This mixture is extracted with successive 5 ml. portions of dithizone until the CCl_4 layer is no longer red. The extracted aqueous solution is extracted again with a few ml. of pure CCl_4 and this CCl_4 is combined with the dithizone extracts. This combined dithizone extract is washed with successive portions of 2% NaOH and distilled water, then transferred to a 25 ml. volumetric flask and diluted to the mark with CCl_4. A 30 minute standing period is suggested in order that full color be produced.

A Cd curve based on extinction coefficients can be prepared with known concentrations of cadmium extracted as described above. The wavelength of maximum absorption for the cadmium dithizonate is 520 millimicrons. Once this curve is drawn it is a simple matter to arrive at concentrations of unknown Cd samples.

If no spectrophotometer is available, however, temporary Cd standards can be made up simultaneously with the water samples using specific cadmium concentrations in the range expected in the samples extracted in the same way. When full color develops, comparisons can be made between the standard and the sample.

The interference of Cu in this determination has not been fully investigated at present. It was found that copper concentrations of less than 0.1 p.p.m. had no effect on the dithizone extraction, but with higher values the cadmium extinction curve could not be used. The range of cadmium concentration for which this procedure is applicable, without concentration or dilution, is about 0.1 to 4.0 p.p.m.

Procedure:

(1) To 50 ml. of a water sample containing 0.1 to 4.0 p.p.m. of cadmium, add 10 ml. of a 10% sodium hydroxide solution.

(2) If arsenic, bismuth, iron, lead, antimony, tin and zinc are likely to be present, 2 ml. of 20% Rochelle salt solution are added.

(3) The sample is then extracted with successive 5 ml. portions of dithizone until the carbon tetrachloride dithizone layer is no longer red.

(4) The sample is extracted finally with U.S.P. carbon tetrachloride and this extraction is added to the combined previous extracts with dithizone.

(5) The combined dithizone extracts are washed with successive portions of 2% sodium hydroxide in distilled water.

(6) The combined washed solvent extract is transferred to a volumetric flask and diluted to the mark with carbon tetrachloride.

(7) After a 30 minute standing period for full color development, color comparisons are made with standards that have been simultaneously prepared similarly. If spectrophotometer is available the extinction values should be read at 520 millimicrons and the cadmium determined by reference to a previously established cadmium curve.

The Determination of Chromium in Water Supplies

For the determination of chromium in the hexavalent state, the method as outlined in Standard Methods for Examination of Water and Sewage, 9th Edition, may be used.

Chromium in the trivalent state very rarely occurs in drinking water supplies and it, therefore, is seldom necessary to resort to another procedure. However, cases may be encountered in water supplies where trivalent chromium has been discharged from plating wastes operation. Other cases may occur where hexavalent chromium has been reduced to the trivalent state by reaction of Cr^{+6} with organic material present in the water under conditions of low pH.

For these reasons it is often necessary to determine not only the hexavalent but also the trivalent chromium present. The total chromium present may be determined by oxidizing the trivalent form to the hexavalent state in either acid or alkaline solution. The oxidation in acid solution may be effected by the use of either ammonium persulfate in sulfuric acid or by the use of potassium permanganate in the same medium. In alkaline solution the oxidation is carried out with bromine according to the New York State Method which has been modified slightly. The perchloric acid method described in the 9th Edition of Standard Methods for the Examination of Water and Sewage is not recommended for total chromium.

OXIDATION IN ACID SOLUTION. REAGENTS REQUIRED:

1. Stock dichromate solution: 0.2829 g. of $K_2Cr_2O_7$ previously dried at 105°C. for one hour is dissolved in distilled water and diluted to one liter. Ten ml. of this solution diluted to one liter makes up the standard solution, each ml. of which is equivalent to 0.0001 mg. of Cr.

2. Sulfuric acid: Concentrated H_2SO_4 is diluted 1:1 with distilled water.

3. Phosphoric acid: 85 per cent H_3PO_4.

4. Ammonium persulfate: 10 g. dissolved in distilled water and diluted to 100 ml.

5. Ammonium hydroxide: The concentrated reagent is diluted 1:1 with distilled water. This should be standardized against the amount of H_2SO_4 used. For example, 5 ml. of 1:1 H_2SO_4 requires about 15 ml. of 1:1 NH_4OH.

6. Manganous sulfate: Dissolve 32 g. of $MnSO_4$ in distilled water and dilute to 100 ml.

7. Silver nitrate: Dissolve 1.7 g. of $AgNO_3$ in distilled water and dilute to 100 ml.

8. Sodium chloride: Use a 10 per cent solution.

9. Sodium sulfite: Dissolve 1.26 g. in distilled water and dilute to 100 ml. One ml. of this solution reduces about 3.4 mg. of Cr^{+6} to Cr^{+++}. This should be freshly prepared each day that it is to be used.

10. Potassium permanganate: Dissolve 0.632 g. of $KMnO_4$ in distilled water and dilute to 100 ml.

11. Diphenyl carbazide: Dissolve 0.2 g. of diphenyl carbazide in 100 ml. of ethyl alcohol. Dilute to 400 ml. with 1:9 H_2SO_4 and store in refrigerator. This reagent is stable for short periods of time only and it is better to make it up in smaller quantities as needed.

OXIDATION IN ALKALINE SOLUTION. REAGENTS REQUIRED:

1. Bromine water: A saturated solution of Br_2 in distilled water.
2. Phenol solution: A 10 per cent solution in distilled water.
3. 2,6-Dibromquinonechlorimide: 0.1 g. is dissolved in 25 ml. of 95 per cent ethyl alcohol. This solution must be kept in a refrigerator. Folin's solution may also be used to test for excess phenol.
4. Asbestos slurry: The asbestos is boiled with 1:1 H_2SO_4 to which a small amount of $K_2Cr_2O_7$ has been added. Filter and wash with distilled water until chromium-free.
5. Sodium carbonate: A saturated solution.
6. Sulfuric acid. Concentrated H_2SO_4 diluted 1:1 with distilled water.
7. Sodium hydroxide: Dissolve 400 g. of NaOH in distilled water and dilute to one liter.

RECOMMENDED PROCEDURES

(A) Alkaline-bromate oxidation (New York State Procedure Modified).

Take two 5 ml. duplicate samples, or samples concentrated to 5 ml. and add two drops of 1:1 H_2SO_4 followed by 3-4 drops of bromine water. Make alkaline with NH_4OH and allow to stand 0.5 hour. After 0.5 hour, add three drops of phenol to the duplicate sample. Remove one drop of treated sample and add one drop of Na_2CO_3 solution followed by one drop of 2,6-dibromquinonechlorimide or Folin's reagent. If an excess of phenol is not present add phenol drop-wise until a positive test is obtained. Add a corresponding amount of

phenol to the other sample, taking into consideration the amount of sample removed from the duplicate for testing for phenol. A slight excess of phenol causes no interference in the subsequent procedure. Filter the sample through a Gooch crucible and wash with distilled water. Add a small piece of litmus paper and make just acid with 1:1 H_2SO_4. Transfer to a 50 ml. Nessler tube. Add 2.5 ml. of diphenyl carbazide reagent and dilute to mark. Compare with standards in five minutes.

If a large amount of organic material is present the oxidation under acid conditions is recommended. However, the above method may be modified as follows to eliminate interference from organic material.

A large excess of bromine water is added to duplicate 5 ml. samples. This is followed by NaOH drop-wise until nearly all of the Br_2 color is destroyed. The solution is then boiled for 10 minutes, acidified with 1:1 H_2SO_4 and most of the Br_2 is boiled off. A second excess of bromine water is added and the mixture boiled until the Br_2 color fades. Add several drops of 10 per cent ammonium persulfate solution and boil off the liberated Br_2. Repeat the persulfate solution additions and boiling until no more Br_2 is liberated. Evaporate to a volume of 5 ml., cool, and proceed as under (A) above.

(B) Ammonium Persulfate-Acid Oxidation.

To the sample add 2 ml. of 1:1 H_2SO_4, 0.2 ml. of H_3PO_4, add one drop of $MnSO_4$ solution and boil until the volume is reduced to 20-25 ml. The Erlenmeyer flasks should be covered with funnels

during the evaporation. Alternately add two drops of $AgNO_3$ solution followed by three drops of ammonium persulfate solution to the gently boiling solution. Allow a little time between the additions for the permanganate color to develop. After development of color add an additional drop of $AgNO_3$ solution and 5-10 drops of persulfate solution and reflux for 10 minutes. Cool and neutralize with the calculated amount of 1:1 NH_4OH solution to slight excess alkalinity. Dilute to 30-35 ml., then evaporate off 6-10 ml. Cool, then add one drop of NaCl reagent and allow to stand for 15 minutes for coagulation of the AgCl. Filter through asbestos using light suction, wash with distilled water, then add one drop 1:1 H_2SO_4. Transfer to 50 ml. Nessler tube and develop color as in (A).

If organic material is present and it is desired to destroy chlorides the above procedure may be modified as follows:

To the sample is added 5 ml. of H_2SO_4 (1:1) and slight excess of sodium sulfite solution to reduce the Cr^{+6} to Cr^{+++}. Allow to stand for several minutes, then evaporate to fumes and fume gently for 4-5 minutes using a funnel to cover the flask. Cool, add one drop of $KMnO_4$ or $MnSO_4$ solution, then warm slightly to destroy the purple color and dilute to about 80 ml. Heat to boiling, then add one drop of $AgNO_3$ followed by ammonium persulfate drop-wise until a purple color appears. Add 5-10 drops more of persulfate and boil for at least 10 minutes evaporating to a volume of about 30 ml. Cool, make alkaline with 15 ml. of

1:1 NH_4OH, then boil until the odor of ammonia is faint. Add one drop of NaCl reagent and allow to cool. Filter, using light suction and develop color as in (A). The method is consistent and gave 98-100 per cent recoveries with 0.005 mg. chromium or more.

(C) Sulfuric Acid-Permanganate Oxidation

To the sample is added 5 ml. of H_2SO_4 and a slight excess of sulfite solution. Allow to stand several minutes. Then evaporate to fumes and fume for five minutes or until clear. During evaporation and fuming keep flask covered with a funnel. Dilute to about 80 ml. and bring to a boil, then add $KMnO_4$ solution drop-wise until a faint pink color appears, then add several drops in excess. Boil for at least 10 minutes or until volume is reduced to 30-35 ml. Cool, add 15 ml. of NH_4OH and boil gently until odor of ammonia is faint. Cool, filter with suction and proceed with color development as in (A).

The purpose of reducing Cr^{+6} to Cr^{+++} with sulfite preceding the evaporation and fuming of sample is to minimize the loss of chromium, the trivalent form being less volatile.

The Determination of Cyanide in Contaminated and Polluted Waters

Collection and Preservation of Samples:

Samples should be collected in a manner to avoid aeration. Sample bottles should be filled completely and stoppered immediately. These samples should be examined as soon as possible after collection, particularly if the concentration of cyanise is small. Samples that must be held for a period of time may be preserved by adjusting the pH of the sample to 11.0 or 12.0 with sodium hydroxide. Samples collected and preserved in this manner can be kept for many days without appreciable loss of cyanide.

Preparation of Samples for Analysis:

The methods for determining cyanides herein described are either colorimetric or require titration to a faint turbidity. Clear, colorless samples are necessary to obtain accurate results. Most stream and sewage samples will have significant turbidity which must be removed prior to making the determination for cyanides.

Polluted surface water samples may be clarified by adding 10 ml. of alumina cream per liter made up in accordance with the directions given in the Ninth Edition of Standard Methods for the Examination of Water and Sewage (1). Serial treatment is usually necessary to obtain satisfactory samples on highly turbid solutions. Sewage may be frequently clarified by the use of 3 ml. of 10 per cent K_3PO_4 per liter of sample This treatment may have to be repeated several times. If buffers are used later in the procedure, the K_3PO_4 may interfere with the cyanide determinations.

Distillation of the sample under acid conditions may accomplish clarification of the sample and concentration of the cyanide. The sample is adjusted to pH 7 with tartaric acid and then acidified with an additional 0.5 gram of the same acid. Fifty or 100 ml. of the distillate is collected in 1 per cent NaOH to avoid loss of cyanide. Certain of the complex and double cyanides are broken down during distillation. Results may, therefore, indicate a higher cyanide content than may be obtained on samples examined without distillation. The readily titratable cyanide, without distillation, is sometimes referred to as free cyanide. The total cyanide includes the complexes broken down by distillation. On the other hand, some cyanide loss may occur during the distillation process. These losses may be due to mechanical losses, losses by oxidation to cyanate, or other compounds, and losses due to hydrolysis.

Qualitative Procedure:

Before making a quantitative determination for cyanides, a qualitative test should be applied to the sample. The prussian blue reaction is specific for cyanides and may be used to detect quantities down to 1 p.p.m. or slightly less. Many modifications of this test exist. The following method may be used:

(a) Make sample alkaline with 1 drop 10% NaOH.

(b) Evaporate 10 or 20 ml. to near dryness.

(c) Add 1 drop of freshly prepared 2% $FeSO_4$.

(d) Acidify with 1 or 2 drops 1-3 H_2SO_4, when cool.

(e) Blue-green color indicates cyanide.

If a prussian blue test is negative, other qualitative tests should be made before the sample is declared to be free from cyanide. Some qualitative tests recommended in the literature are the o-cresolphthalin [2], and the benzidine-copper acetate test [3].

Quantitative Procedures:

Four quantitative procedures are recommended depending upon the concentration of cyanide and the interfering substances in the samples:

A. The pyridine-benzidine method is recommended for cyanide concentrations of .01 to 1.0 p.p.m. Due consideration for interfering substances must be taken into account.

B. A modified Liebig Method can be used for cyanide concentrations over 1 p.p.m.

C. The Liebig method using an internal indicator for cyanide concentrations of 1 to 10 p.p.m.

D. The prussian blue method should be used for cyanide concentrations between 10 and 100 p.p.m. where substances are encountered which interfere with the former methods.

(A) PYRIDINE-BENZIDINE METHOD [4]

Apparatus: Spectrophotometer or other photoelectric instrument to measure at wavelength of 520 millimicrons, 100 ml. Nessler tubes.

Reagents: Acetic acid, glacial.
Bromine water - saturated.
Sodium arsenite (Meta) 1.5% aqueous.

Reagents: Pyridine benzidine dihydrochloride reagent prepared by making a 2% solution of the benzidine salt in pyridine which contains 2 ml. of concentrated hydrochloric acid per 100 ml.

Standard cyanide solution. From a batch of potassium cyanide previously analyzed by the Liebig Method, a solution is made containing 1 mg. per liter of KCN. Two, 4, 6, 8, 10 and 12 ml. samples of the standard were used.

Procedure:

Samples should contain from 0.002 to 0.02 mg. KCN. Acidify the sample to litmus with a small excess of acetic acid and add 0.2 or 0.3 ml. of saturated bromine water. Add 0.5 ml. of 1.5% sodium arsenite, or enough to neutralize excess bromine as evidenced by disappearance of bromine water color. Add the treated sample to the pyridine-benzidine reagent and let stand 10 minutes. Dilute to 100 ml. and read the red color after 10 but before 30 minutes, either visually or with a spectrophotometer at wavelength of 520 millimicrons. Compare reading with standards treated in the same manner.

Interfering Materials:

Copper was found to interfere if present in amounts of 10 p.p.m. or more. Iron and lead interfere in concentrations of over 100 p.p.m. and zinc can be tolerated up to 250 p.p.m. Small amounts of oxidizing and reducing agents do not interfere and it is reported that phosphate, chloride, oxalate, borate and ethyl alcohol have no effect.

(B) MODIFIED LIEBIG METHOD

This method for the determination of cyanide is generally reliable and has been in use for many years. The analysis is based on the fact that silver nitrate forms a soluble double cyanide with an alkali cyanide. When all the cyanide has been converted to the double salt, further additions of silver produce a permanent turbidity due to precipitation of silver cyanide. The addition of potassium iodide causes the yellowish silver iodide to be precipitated, thus making the difficult endpoint more readable.

Apparatus: Burette, 25 or 50 ml.
Erlenmeyer flasks, 250 ml.
Light source, beam type.

Reagents: Silver nitrate, 0.1 N and 0.01 N.
Sodium hydroxide, 10%.

Procedure:

A volume of sample is selected so as not to require over 10 or 15 ml. of the silver nitrate solution. Samples containing from 1 p.p.m. to several thousand p.p.m. may be examined by this method. Add 10 ml. of the KI solution and 1 ml. of the sodium hydroxide solution to the sample and dilute to 100 ml., or if cyanide is present in very low concentration, 250 ml. of the sample may be used. If the sample is turbid, filter before starting the titration. Titrate with 0.1 N or 0.01 N $AgNO_3$, depending on the concentration of cyanide present, to a faint turbidity. On dilute solutions the endpoint is a faint opalescence and difficult to see. A concentrated source of light, such as that furnished by a microscope lamp, and a black surface under the flask are aids in detecting the endpoint.

(C) MODIFIED LIEBIG METHOD USING AN INTERNAL INDICATOR

The Liebig method for the determination of cyanides has not been found practicable in the presence of cyanide concentration of 1 to 10 p.p.m. or less due to the difficulty of reading the faint turbidity at the endpoint. Greater difficulty is experienced in the presence of natural turbidity. Ryan and Calshaw [5] have proposed the use of p-dimethylaminobenzylidenerhodanine as an internal indicator in connection with the Liebig Test for the determination of cyanide. The use of this indicator has been adapted to cyanide determinations on polluted waters and industrial wastes.

The indicator p-dimethylaminobenzylidenerhodanine

has the property of forming colored salts with silver and certain other heavy metals.

Generally the reactions with the indicator and silver are carried out in acid solution. However, in cyanide determinations the reaction is satisfactory in alkaline solution unless heavy metals are present. Samples for the determination of cyanide usually do not contain appreciable quantities of heavy metals, or, as in certain industrial wastes, heavy metals are removed by distillation prior to the analytical determination of cyanide.

When a solution of silver nitrate is added to that of a cyanide, $Ag(CN)^-_2$ is formed. This complex ion is soluble in the excess of cyanide and no precipitate is formed. The $Ag(CN)_2$ is very slightly ionized particularly in alkaline solution and the silver ions do not react with the indicator. When enough silver has been added to unite with all the cyanide, $Ag(Ag(CN)_2)$ is formed. This compound is ionized sufficiently to permit the reaction of the indicator and the silver ions. A change from the yellow color to a salmon pink color is noted at the endpoint.

Comments:

This method has been found satisfactory on Ohio River and Little Miami River waters which were dosed with cyanide in concentrations from 0.5 to 12.0 p.p.m. A .001N silver nitrate solution was used. Turbid samples which could not be determined by the ordinary Liebig method were easily determined using the indicator. River water samples flocculated upon addition of the NaOH and could be clarified by filtering although this was not usually done. The method was used on an industrial waste which had been made alkaline to phenolphthalein, treated with 5 per cent lead acetate solution and filtered. The waste was then made acid with tartaric acid and distilled into 2 per cent NaOH. Increments of cyanide added to the original sample were recovered quantitatively.

The pH should be 10.5 to 12.0. An amount of indicator sufficient to get a sharp endpoint should be used. Eight drops of indicator per 100 ml. of sample was satisfactory in the tests made. A yellow color of sufficient intensity to obscure the first appearance of the salmon pink endpoint should be avoided.

Procedure:

1. Adjust the pH of a 100 ml. sample to between 10.5 and 12.0 with 10 per cent NaOH.
2. Add 8 drops of indicator. The indicator is prepared by dissolving ~~0.2~~ .02 g. of p-dimethylaminobenzylidenerhodanine in 100 ml. of acetone.
3. Titrate sample with .001N $AgNO_3$ to first appearance of salmon pink color.
4. Add 8 drops of internal indicator to a volume of distilled water equal to the sample and titrate with $AgNO_3$ for a blank titration.
5. Deduct blank titration in (4) from sample titration in (3) to obtain $AgNO_3$ used by cyanides.

Calculation:

1 ml. of .001N $AgNO_3$ = .052 mg. CN^-

(D) PRUSSIAN BLUE METHOD

Many modifications of this test for cyanides exist. Essentially the method consists of treatment of the alkaline sample to be analyzed with minute amounts of ferrous sulfate followed by acidification. One of the modifications that gave usable results in a narrow range follows:

Apparatus: 100 ml. Nessler tubes.

Reagents: Sodium hydroxide, 10%.

Ferrous sulfate, saturated, freshly made.

One drop of concentrated sulfuric acid added to the solution will keep it for 3 or 4 hours.

Potassium fluoride, 10%.

Sulfuric acid - 1 to 3.

Standard cyanide solution containing 100 p.p.m. KCN. Use 2, 4, 6, 8 and 10 ml. portions.

Procedure:

Five or 10 ml. samples containing from 2 to 10 mg. of KCN are satisfactory.

Adjust pH of sample to pH of about 12.0 with sodium hydroxide. Add 0.2 ml. of freshly prepared saturated solution of ferrous sulfate. Add 0.5 ml. of 10% KF solution. Let stand 5 minutes. Acilify with 1 to 3 sulfuric acid. The 2, 4, 6, 8 and 10 ml. portions of the cyanide standard solution are treated the same way. All samples and standards are then diluted to 100 ml. Visual readings may be made after 30 minutes. More accurate results were obtained by the use of Beckman Model DU Spectrophotometer. Readings were made at a wavelength of 710 millimicrons, using a 10 cm. cell.

Interfering Materials:

Double cyanide and iron cyanogen compounds are not measured by the method. This method is considered useful only in the range of 10 p.p.m. to 100 p.p.m. of CN. Once the color is formed it is stable. Readings may be made at any time from 30 minutes to several hours. It is to be remembered that the blue color is actually a fine precipitate and samples should be thoroughly agitated and read rapidly.

Literature on Cyanides

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